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Processing, Microstructure, and Strength of Alumina–YAG Eutectic Polycrystals

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Dense polycrystalline eutectics of alumina and yttrium aluminum garnet (YAG) were fabricated by hot-pressing powders of pulverized arc-melted buttons at homologous temperatures of $0.9T_{eu}$–$0.93T_{eu}$ (where T_{eu} is the eutectic temperature). The eutectic microstructure of the arc-melted buttons was retained after densification, although the grain boundaries were decorated with equiaxed grains of alumina and YAG ~1–5 μm in size; possible causes for their formation have been discussed. A comparison of the measured strength of the polycrystalline eutectics (274 ± 61 MPa) with grain size and fracture toughness suggests that the strength-limiting flaws are significantly smaller than the mean grain size and larger than the mean eutectic spacing.

I. Introduction

PREVIOUS work[1–4] on directionally solidified (DS) bulk material and fibers of the alumina–yttrium aluminum garnet($Y_3Al_5O_{12}$, YAG) eutectic (AYE) has uncovered several interesting properties that also may provide advantages in the form of polycrystals. Directionally solidified product (DS-AYE) possesses excellent morphologic stability to temperatures near the eutectic temperature (T_{eu}) of 1826°C.[1,5–7] The creep resistance of DS-AYE is better than α-oriented sapphire,[8] because of the reinforcement of the sapphire matrix by the YAG phase, which is the most creep-resistant oxide known.[9] The DS-AYE also has a relatively higher fracture toughness (via the single-edge notched beam (SENB) method) than sapphire or YAG, and, more importantly, the fracture toughness remains independent of temperature.[1] The AYE fibers, which are grown using the edge-defined film-fed growth (EFG) technique, routinely exhibit high room-temperature strength (>2 GPa).[3,4,10] A significant conclusion of our AYE fiber work has been that the fiber strength is independent of the fiber diameter.[2] Note that this observation is contrary to that by Kennard *et al.*,[11] Hulse and Batt,[12] and Stubican and Bradt,[13] who reported that the strength of the MgO–$MgAl_2O_4$, ZrO_2–$CaZrO_3$, and ZrO_2–MgO eutectics, respectively, was dependent on the colony size. Instead, a good correlation was observed between the fiber strength and the scale of the eutectic phases (σ_f, which is approximated by the inverse square root of the eutectic spacing).[3,4] Thus, for the AYE system, it is possible that, in polycrystalline form, the scale of the eutectic phases, rather than the grain size, determines the strength.

If, in AYE, the grain size does not influence the strength, it may be possible to obtain an unusual combination of high strength and high creep resistance within a polycrystalline microstructure. This observation suggests that such eutectic polycrystals could provide the basis for a new family of affordable materials for high-temperature structural applications. However, the melting point of the AYE eutectic is much lower than the constituent compounds; yet, the consolidation temperature of the eutectic polycrystals can be expected to be almost the same as that of the single-phase powders, i.e., at a very high homologous temperature. Thus, consolidation of AYE eutectic powders to polycrystals without losing the desired microstructure may be difficult. Rice,[14] Krohn *et al.*,[15] and Homeny and Nick[16] reported on the fabrication of alumina–partially stabilized zirconia eutectics from ceramic eutectic particles. However, YAG is significantly more creep-resistant than ZrO_2 and has a much lower melting point ($T_m \approx 1940$°C) than ZrO_2; therefore, the processing of AYE without microstructural coarsening can be challenging.

The present work is the result of a preliminary evaluation of the feasibility of processing polycrystalline AYE oxide for structural components. Limited flexural-strength test data and their relationship to microstructural length scales are reported, in comparison with previous results on eutectic fibers and DS eutectics.

II. Experimental Procedure

Alumina (Type AKP-53, >99.99% pure, Sumitomo Chemical Co., Ltd., Tokyo, Japan) and yttria (>99.999% pure, Rare Earth Products, Johnson Matthey, Ward Hill, MA) powders were mixed in the eutectic composition (66.5 wt% Al_2O_3 and 33.5 wt% Y_2O_3)[17] with a magnetic stirrer in deionized water. The powder mixture was uniaxially pressed into pellets (2.54 cm in diameter, ~2 cm thick) and sintered at 1500°C for 2 h in air. The sintered pellets were arc-melted three times on a water-cooled copper hearth and turned over after each melting, to obtain chemical homogeneity. After arc melting, a piece of the pellet was sectioned for microstructural analysis, and the rest of the button was crushed into pieces <5 mm in size. (The buttons were too porous and too severely cracked to be used directly for evaluation of the polycrystals.) Final pulverization was accomplished using a shatterbox (SPEX CertiPrep, Inc., Metuchen, NJ) with a zirconia grinding container. The pulverized powder was sieved through a 100 mesh (~150 μm) nylon sieve (SPEX CertiPrep, Inc.) to avoid metal contamination, and then the particle-size distribution of the sieved powder was measured (Model LS 230, Coulter Corp., Hialeah, FL).

AYE powder from arc-melted buttons was vacuum-hot-pressed uniaxially in a graphite die (inner diameter of 2.54 cm) that was lined with molybdenum foil. The hot-pressing temperatures were 1600°–1700°C, at a pressure of ~20 MPa for 15 min. After hot pressing, the density of the AYE polycrystal was measured using the Archimedes method. A sample of the fine powders also was heat-treated in a fashion that simulated hot pressing at 1650°C, to observe their morphologic evolution, for comparison to the hot-pressed specimens.

The uniformity and scale of the microstructures of the specimens were examined via scanning electron microscopy (SEM) (using secondary and backscattered electron imaging (BEI)) and energy-dispersive X-ray spectroscopy (EDS) analysis. The sectioned hot-pressed specimens were mounted both parallel and perpendicular to the hot-pressing direction and polished to a 1 μm finish, using a final polish of 0.05 μm γ-alumina in a vibration polisher (Model Vibromet I, Buehler, Lake Bluff, IL). The

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polished specimens were thermally etched (with heating and cooling rates of 5°C/min) at 1400°–1500°C for 15 min in air, to reveal the structure at and near the grain boundaries. Computer imaging software (NIH Image) was used to determine the eutectic spacing of the AYE polycrystals.

The flexural strengths of the polycrystals were evaluated using rectangular bars machined from AYE polycrystals that had been tested in four-point bending. The nominal dimensions of the specimens were 2.2 mm × 4 mm × 25 mm. The tensile surface and rounded edges of the bend bars were polished manually to a surface finish of 0.05 μm. The bend tests (approximately fifteen tests) were performed under displacement control in a screw-type tensile testing machine (Model Sintec® 20/G, MTS, Research Triangle Park, NC) at a displacement rate of 127 μm/min (0.005 in./min). The standard beam theory was used to calculate the flexural strength from the maximum load.

III. Results and Discussion

Two different microstructural regions are clearly evident in the SEM photomicrographs of a typical as-arc-melted button (Fig. 1(a)) and the AYE polycrystals that were made from pulverized as-arc-melted stock (Fig. 1(b)). Except for a small degree of spheroidization (which was observed at high magnification), the general eutectic microstructure of the as-arc-melted button was retained after pulverization and hot pressing, despite hot pressing at a homologous temperature of $0.93T_{eu}$. The scale of the eutectic lamellae varied considerably (from <1 μm to >10 μm), presumably because of cooling-rate variations at different places in the button. A slightly greater degree of spheroidization was evident in the AYE polycrystals that were hot-pressed at 1700°C than in those hot-pressed at 1600°C. The 1700°C hot-pressed specimens were theoretically dense, whereas the 1600°C hot-pressed samples contained a few percent of porosity. No significant microstructural difference was noticed on the specimens that were mounted either parallel or perpendicular to the hot-pressing direction.

Typical SEM photomicrographs of thermally etched AYE polycrystals are shown in Fig. 2. The microstructure is unusual in that large grains of eutectic microstructure have a layer of small equiaxed and large grains between them. These regions at the boundaries between the larger grains (~100 μm) ranged in thickness from a few micrometers to a few tens of micrometers and contained grains of alumina and YAG (0.5–5 μm in size). Possible mechanisms for the development of the microstructure are discussed later in this work.

The average flexural strength of the polycrystals (based on fifteen tests) was 274 ± 61 MPa. If the size of the strength-limiting flaws is assumed to be the same as the grain size, for grain sizes of 150 μm (maximum) and 100 μm (mean), this strength translates to fracture toughnesses ($K_{IC} = 1.1\sigma(\pi a)^{0.5}$) of 6.5 and 5.3 MPa·m$^{0.5}$, respectively. The fracture toughness (via the SENB method, using a notch width of 0.25 mm) of the DS-AYE was reported to be 4.3 MPa·m$^{0.5}$.[1] The fracture toughnesses that were measured using smaller notch widths, indentation cracks, or the double cantilever beam (DCB) method are all likely to be even lower (by >20%).[18,19] Clearly, the size of the strength-limiting flaw is significantly smaller than the mean grain size.

To examine if the size of the strength-limiting flaw correlates with the eutectic spacing, the strength data were compared with those of single-crystal AYE fibers and DS eutectics, which have been reported elsewhere.[1,3] Figure 3 is a plot of the strength versus microstructural-scale size for the various AYE eutectics. For each strength datum, three microstructural dimensions were considered: grain size, colony size, and eutectic spacing. For the fibers, the eutectic spacing is the only parameter, and, for the polycrystals, the colony size is the same as the grain size. Figure 3 shows that the strength of the fibers varies as the inverse square root of the eutectic spacing, with an effective fracture toughness of K_{IC} = 2.3 MPa·m$^{0.5}$. Figure 3 includes the collected data on polycrystalline Al_2O_3.[20] The behavior of AYE fibers seems to agree well with that of fine-grained polycrystalline Al_2O_3, both plotting along a single straight line. If this line is compared with the data of DS-AYE and the AYE polycrystals, Fig. 3 shows that, for these materials, the grain size is too large and the eutectic spacings are too small. The former (the grain size being larger) is consistent with the previously discussed analysis. The eutectic spacing was in the range of ~1–10 μm (see Fig. 1(b)); thus, the larger of this distribution might be appropriate to consider for strength-limiting size. However, even this value is not large enough to rationalize the data. Processing flaws that are intermediate in size between the spacing and the grain size are more likely to be strength limiting. SEM fractographic analyses have revealed that, in at least some of the specimens, the fractures originated from large and/or small cluster of pores or large clusters of small alumina grains; these flaws varied in size but all were less than ~40 μm. The above discussion suggests that the strength of AYE eutectic polycrystals is limited by the eutectic spacing or processing-induced flaws (smaller than the grains), rather than the grain size.

The regions of mixed grain structure between large eutectic grains may influence the properties significantly, most likely in a detrimental fashion. Thus, control and/or elimination of their formation will be important in the optimization of the material.

A possible mechanism of formation is based on the natural packing of very small powder particles between much-larger particles. The small particles then spheroidize during processing, in part because they are too small to possess the stabilizing eutectic microstructure. The particle-size analysis for the −100 mesh AYE powder shows a bimodal distribution, with a median particle size of ~40 μm, whereas a significant fraction (>5 vol%) are very fine (<1 μm) and more than 10 vol% of the powder grains have a grain size of >100 μm. The finer particles are approximately the same size as the smaller dimension of the phases within the eutectic structure. Thus, a scenario (experimentally observed in Fig. 2) is suggested, wherein the finer particles that are entrapped between larger particles sinter to a region of equiaxed two-phase microstructure. The formation of large grains in these regions may be due to the entrapment of large eutectic phases in the arc-melted button and also the grain growth of connected alumina–alumina and YAG–

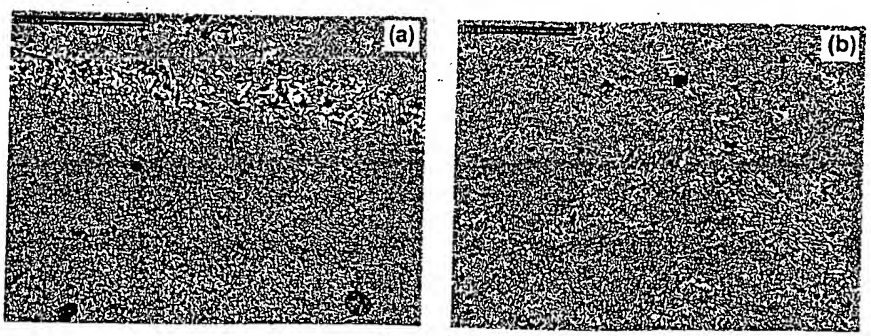

Fig. 1. SEM (BEI) photomicrographs of (a) as-arc-melted AYE button (bar = 200 μm) and (b) AYE polycrystal hot-pressed at 1650°C (bar = 100 μm).

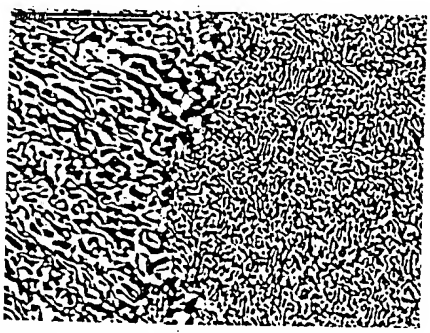

Fig. 2. SEM (BEI) photomicrograph of AYE polycrystal subjected to thermal etching (1400°C for 15 min in air), showing small (~1 μm) and large (~5 μm) grains of Al_2O_3 and YAG at the grain boundary. Bar = 20.0 μm.

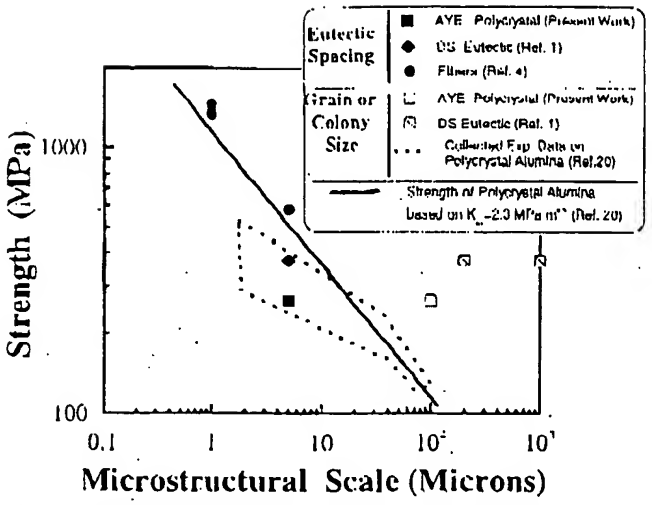

Fig. 3. Strength as a function of lamellae scale for various AYE eutectics. Data were taken from Mah and co-workers,[1–4] Mukhopadhyay *et al.*,[19] and Rice[20] and compared with data from the current study.

YAG particles. Some of the finer particles have been collected and subjected to a heat treatment at the hot-pressing temperature. They show spheroidization similar to that observed in the polycrystal. Interestingly, the lamellar grains do not coarsen, consuming the small grains during processing. One possible reason for this observation is that the lamellar structure at the grain boundary has interfaces with radii of curvature that are comparable to those of equiaxed grains, which decreases the driving force for grain growth.

The second possible mechanism is that, during hot pressing, localized high stresses that are generated at the surfaces of the particles cause significant deformation, followed by surface recrystallization, which results in grains of alumina and YAG. Generally, it is believed that, during the initial stages of hot pressing, powder particle rearrangement occurs via particle sliding, aided by fragmentation and plastic flow;[21] hence, localized stresses could be high enough to cause recrystallization in smaller particles. Formation of sub-boundaries has been reported in yttrium iron garnet (YIG) single crystals that have been deformed in the temperature range of $0.8T_m$–$0.9T_m$.[22] Extensive plastic deformation of single-crystal YAG at 1600°C under indentation compression also has been reported.[23] Thus, it seems reasonable that the surfaces of the large particles underwent large plastic deformation during hot pressing (at $>0.9T_{eu}$) and recrystallized at the surface as equiaxed grains of alumina and YAG. A third possibility is that the eutectic phase spheroidizes at the surface of the particles during the high-temperature exposure; however, transmission electron microscopy (TEM) analysis of the grains at the boundary region, according to Cinibulk,[24] did not reveal them to have the same orientation as the adjacent lamellae in the grains.

The first mechanism would suggest that the fines in the powder be removed (e.g., the production of almost-monosized powder with a small and uniform eutectic microstructure via rapid solidification processing) before consolidation, to eliminate the equiaxed regions, whereas the latter mechanism would suggest that it would be necessary to perform pressureless sintering or hot pressing at lower pressures, to minimize high stresses. Such experiments should clarify the formation mechanism.

IV. Summary and Conclusions

Polycrystals with grains of a eutectic microstructure (alumina–yttrium aluminum garnet (Al_2O_3–YAG)) were fabricated by hot pressing −100 mesh (<150 μm) powders of a eutectic structure at homologous temperatures of $0.9T_{eu}$–$0.93\ T_{eu}$ (where T_{eu} is the eutectic temperature). The polycrystals were very dense, with a grain size that was almost the same as the powder size. The eutectic microstructure was almost fully retained. However, a certain degree of spheroidization of the eutectic phases was observed, and the degree of spheroidization was greater for higher hot-pressing temperatures. Furthermore, the grain boundaries were decorated with small equiaxed grains of Al_2O_3 and YAG. Two mechanisms were proposed for the formation of the boundary regions, along with strategies to avoid them. A comparison of the measured flexural strength to grain size and fracture toughness suggests that the strength-limiting flaws are significantly smaller than the grain size but larger than the eutectic spacing, which indicates the presence of intermediate-sized processing flaws. This work indicates that such structures merit further investigation for high-strength, creep-resistant oxide materials that can be consolidated using conventional processing approaches for ceramic powders.

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